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THE STRUCTURE OF BIS-PYRIDINE METAL DIHALIDE COMPLEXES

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Abstract—The structures of complexes of the type M^{II} $(Hal)_2$. 2 Pyridine have been investigated by a variety of physical techniques. Particular attention has been paid to the cobalt complexes which can exist in one or both of two isomeric forms. The factors which decide whether the tetrahedral monomer or octahedral polymer form will be the more stable are discussed. By using various metals five different types of complexes of the above formula have been identified — (a) tetrahedral monomer; (b) octahedral polymer; (c) square planar monomer; (d) tetragonal polymer; (e) (presumably) irregular tetrahedral monomer. The influence of the electronic configuration of the metal and the effect of the ligand on the structure adopted are discussed.

MOST of the metals of the first transition series form complex compounds having the general formula $M^{II}X_2$. 2Pyridine, where X is a halogen or a pseudo halogen (e. g. — NCS) atom. Some of these compounds exist in two different forms which differ markedly in colour and in other physical properties. The best known example of this isomerism is provided by the compound $CoCl_2$. 2Py which can exist at room temperature both as a violet (stable) form and also as a blue (unstable) modification. With some halogen (or pseudo halogen) atoms either the so-called violet or the blue form only have been prepared. Thus CoI_2 . 2Py is known only as the blue form whereas $Co(NCS)_2$. 2Py has been prepared only as the so-called violet form, at least in the solid state, since the blue form of the latter exists in certain solvents. Some years ago one of us (T. C.) set out to study the structure of the blue and violet forms of $CoCl_2$. 2Py, there being considerable uncertainty as to these at the time. Whilst the investigation was in progress crystal structure studies on the violet form and on a related blue form provided strong confirmation of our conclusions but since there is confusion in the literature concerning the structure of complexes of the type $M^{II}X_2$. 2Py in general we widened the scope of the investigation to a study of complexes of this type as a whole. In particular, the effect on structure caused by varying the metal and the halogen atom have been investigated and the former is correlated with the number of non-bonding *d* electrons in the metal atom. In addition it has been found possible to interpret published work on similar types of complexes using other ligands.

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Several obvious stereochemical arrangements are feasible for complexes of the type $M^{II}(hal)_2 . 2Py$. If the co-ordination number of the metal atom is *four* the possible arrangements are square planar (*cis* or *trans*), regular tetrahedral and irregular tetrahedral (e. g. with a lone pair in the valency shell as in $TeCl_4$). The co-ordination number *six* requires polymerization with a halogen bridge, a typical structure being as shown in Fig. 1. For a co-ordination number *five* a simple dimer is required; such an arrangement is at least feasible for a complex of the type $SnCl_2$. 2ligand since the presence of a lone pair on the tin atom is expected to limit polymerization beyond the dimer stage. In the above formulations it is assumed that the compound is a non-electrolyte since the structure $[M^{II}Py_4]M^{II}X_4]$ has the same empirical formula.

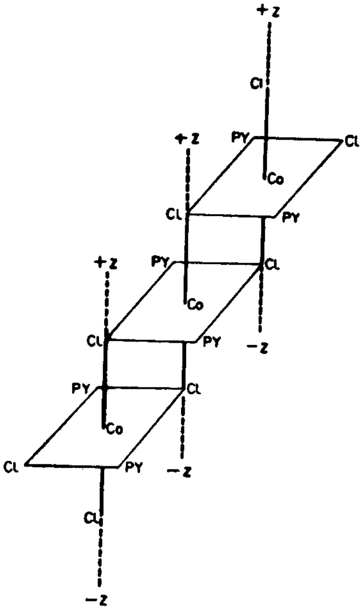

FIG. 1.—Structure of violet form of $CoCl_2$. 2Py.

As a background it is convenient to discuss first the structure of the two forms of $CoCl_2 . 2Py$. In 1894⁽¹⁾ it was shown that cobaltous chloride and pyridine react to form the violet $CoCl_2 . 2Py$ complex whilst the blue isomer was first prepared in 1927 by HANTZSCH⁽²⁾ by treating a solution of the violet form in chloroform with petroleum ether. The blue form reverts to the violet on standing in air for a few hours; the change-over is autocatalytic, being accelerated by the presence of moisture. Before 1939 a number of other investigators⁽³⁾ had studied these two isomers using

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(1) F. REITZENSTEIN, *Liebigs Ann.* **282**, 273 (1894).

(2) A. HANTZSCH, *Z. Anorg. Chem.* **159**, 273 (1927).

(3) (a) E. G. COX, A. J. SHORTER, W. WARDLAW and W. J. R. WAY, *J. Chem. Soc.* 1556 (1937); (b) E. D. P. BARKWORTH and S. SUGDEN, *Nature, Lond.* **139**, 374 (1937); (c) D.P. MELLOR and B. S. MORRIS, *J. Proc. Roy. Soc. N. S. W.* **71**, 536 (1938).

cryoscopic and magnetic measurements and also a partial single crystal X-ray examination of the violet form had been carried out. Conflicting conclusions were arrived at but MELLOR and CORYELL(4) on the basis of magnetic measurements alone appear to have been the first workers to suggest the correct structures. They suggested that on the basis of the colour, the blue form was a tetrahedral monomer both in the solid state and in solution and that the violet form was probably polymeric. Both forms were regarded as "ionic" (spin-free) containing three unpaired electrons but the implications of the difference in orbital contribution to the magnetic moment were not discussed. As recently as 1950, however, SIDGWICK(5) favoured *cis–trans* isomerism in a square complex to explain the existence of two forms but he pointed out that the difference in the magnetic moments of the two forms was not easy to explain. It is now recognised that in any case square co-ordination would lead to one unpaired electron and not three as is observed.

In our investigation the violet form was prepared by the method of REITZENSTEIN(1). The compound was fairly stable for several months in a stoppered tube but a little loss of pyridine slowly took place. However, the compound absorbs moisture rapidly if freely exposed to the atmosphere, with rapid loss of pyridine under these circumstances. The solid blue form may be obtained from hot alcohol or by heating the violet solid at 120°C for several hours.(3a) It is also obtained by removing the solvent from a chloroform solution of the violet form leaving bright blue crystals.(3a) The preparation of the blue form as suggested by HANTZSCH(2), involving precipitation of the compound from a chloroform or bromoform solution with petroleum ether is inconvenient because of the ease with which transformation to the violet form occurs. All preparations of the blue form reverted to the violet on standing but the transition is much slower in a dry atmosphere; this was confirmed by X-ray analysis. When soluble the blue and violet forms dissolve to give blue solutions in organic solvents, the absorption spectra being identical. The spectra in nitrobenzene of the complexes $CoCl_2 . 2Py$, $CoBr_2 . 2Py$ and $CoI_2 . 2Py$ are shown in Fig. 2. It may be seen that the extinction coefficients are very large when compared with the simple *d-d* bands observed in octahedral complexes. This behaviour parallels that shown by the $[CoCl_4]^{2-}$, $[CoBr_4]^{2-}$ and $[CoI_4]^{2-}$ ions. The position of the maxima steadily move towards longer wavelengths as we pass from the chloride through the bromide to the iodide (as also occurs with the tetrahalides) presumably due to the fact that the crystal field strength decreases along this sequence. Recently the spectrum of $CoBr_2 . 2Py$ in bromoform has been studied and discussed by FERGUSON(6) and the ϵ_{max} values observed agree well with those given in Fig. 2 although there is some difference in the values of λ_{max}. KATZIN(7) has also reported the spectrum of $CoCl_2 . 2Py$ in various solvents but the values of λ_{max}

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(4) D. P. MELLOR and C. D. CORYELL, *J. Amer. Chem. Soc.* **60**, 1786 (1938).

(5) N. V. SIDGWICK, *Chemical Elements and their Compounds* p. 1386. Oxford University Press (1950).

(6) J. FERGUSON, *J. Chem. Phys.* **32,** 528 (1960).

(7) L. I. KATZIN and E. GEBERT, *J. Amer. Chem. Soc.* 75 2830 (1953).

which he observed in benzene, chloroform, acetone and isopropyl alcohol also differ from those in nitrobenzene; log ϵ values quoted were relative only. Reflexion spectra of the two forms of $CoCl_2 . 2Py$, $CoBr_2 . 2Py$ and $CoI_2 . 2Py$ have also been examined.(6,7) The complexes dissolve in water with decomposition, the characteristic pink colour of the hexa-aquo cobaltous ion being observed.

Molecular weight measurements in nitrobenzene and in chloroform(3a) and bromoform(3c) show that irrespective of whether one starts with the blue or the violet form the solute is monomeric. In nitrobenzene the solute is a non-electrolyte. These data indicate the presence of a monomer $[CoCl_2 . 2Py]^0$ in solution and since there is no evidence for the existence of the violet form in any solvent the latter appears to be a polymer which breaks down on dissolution. (The formula $[CoPy_4]$ $[CoCl_4]$ can be excluded on the basis of colour and magnetic data.)

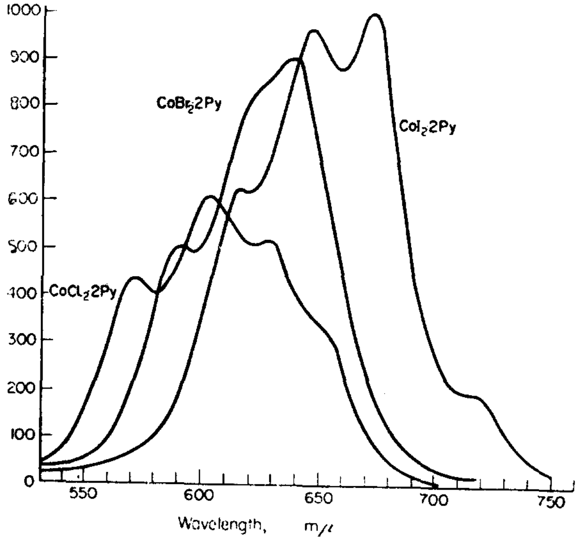

FIG. 2.—Absorption spectra of $CoCl_2 . 2Py$, $CoBr_2 . 2Py$ and $CoI_2 . 2Py$, 0·0005 M in nitrobenzene

To confirm the hypothesis of stereochemical change on solution the magnetic susceptibility of the blue and violet forms in the solid state and in solution have been determined. Data for the solid state agree in general with previous workers(3b) but the solution data are reported for the first time. As has been discussed elsewhere,(8) the magnetic moments of tetrahedral Co(II) complexes usually lie in the range 4·4–4·8 B.M., whilst those of octahedral complexes are higher (4·8–5·2 B.M.), the orbital contribution being larger in octahedral complexes. The expected μ_{eff} in tetrahedral complexes is increased above the spin only value of 3·88 B.M. by a factor $\left(\frac{1 + 4\lambda^1}{\Delta}\right)$ owing to spin-orbit coupling. (In this expression λ^1 is the effective spin-orbit coupling constant and Δ is the $d_\epsilon - d_\gamma$ separation). The value of λ^1 is very

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(8) B. N. FIGGIS and R. S. NYHOLM, *J. Chem. Soc.* 12 (1954); 338 (1959).

much dependent upon the nature of the attached ligands. The data in Table 1 indicate that the violet form is an octahedral, presumably polymeric, complex and that the blue form is a tetrahedral monomer as originally proposed by MELLOR and CORYELL(4). Confirmation of this has been provided by X-ray studies. DUNITZ(9) has shown that the violet form has the structure shown in Fig. 1, involving bridging chlorine atoms. Support for the view that the blue form is tetrahedral may be

TABLE 1.—MAGNETIC MOMENTS OF $CoX_2.2Py$ COMPLEXES*

Solid substance	μ_{eff} (B.M.)(20°C) of Solid	μ_{eff} (B.M.)(20°C) (in $PhNO_2$ solution)	Colour of solution
$CoCl_2.2Py$ Violet	5·15	4·52	Blue
$CoCl_2.2Py$ Blue	4·42		
$CoBr_2.2Py$ Blue	4·50	4·52	Blue
$CoI_2.2Py$ Blue	4·47	4·59	Blue
$Co(NCS)_2.2Py$ Purple red	5·10	4·50	Blue
$Co\ Py_2Br_2.2H_2O$ Violet	5·00	4·56	Blue

* For comparison the magnetic moments of the tetrahedral $[CoCl_4]^{2-}$ $[CoBr_4]^{2-}$ and $[CoI_4]^{2-}$ ions are 4·69 4·74 and 4·85 B. M. respectively, whilst those for the octahedral $[Co(H_2O)_6]^{2+}$ and $[Co(NH_2)_6]^{2+}$ ions are in the range 5·0–5·1 B. M.

inferred from the fact that the blue compound Co_2 . 2Aniline is tetrahedral as also are CoI_2 . 2*p*-toluidine Co_2 . 2*p*-toluidine and $CoCl_2$. 2*p*-iodoaniline.(10) According to LYASHENKO(11) the blue forms of $CBrCl_2$. 2Py and $CoBr_2$. 2Py are isomorphous. Finally PORAI-KOSHITS(12) refers to unpublished work which indicates that the blue form of $CoCl_2$. 2Py is tetrahedral.

It is now of interest to examine the properties of other cobalt compounds with the same general formula. The stable forms of $CoBr_2$. 2Py and CoI_2 . 2Py are blue and have moments which indicate tetrahedral arrangements (see Table 1). The violet forms of these two substances appear not to have been isolated. The low conductivities of these compounds in nitrobenzene indicate that they are non-electrolytes in

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(9) J. D. DUNITZ, *Acta Cryst.* **10**, 307 (1957).

(10) T. I. MALINOVSKI, *Kristallografiya* **2**, 734 (1957).

(11) M. N. LYASHENKO, *Kristallografiya* **1**, 361 (1956).

(12) M. A. PORAI-KOSHITS, *Zh. Neorg. Khim.* **4**, 730 (1959).

this solvent whilst the magnetic moments show that the compound is unchanged on dissolution indicating that it is tetrahedral.

The properties of certain related compounds are of interest. The dihydrate $CoPy_2Br_2 . 2H_2O$ is formed when $CoBr_2 . 2Py$ is left in moist air. It is violet in colour suggesting octahedral co-ordination in the solid state and this is supported by the magnetic moment of 5·0 B.M.; however, on dissolving this substance in nitrobenzene the moment falls to the value corresponding to tetrahedral co-ordination and the conductivity is small enough to indicate a non-electrolyte. The absorption spectrum in nitrobenzene is identical with that of tetrahedral $CoBr_2 . 2Py$ showing that the two molecules of co-ordinated water are lost on dissolving the compound in nitrobenzene.

It is of interest to compare the three halides in regard to their capacity to form six covalent derivatives. Whilst the dichloride forms both the violet octahedral and blue tetrahedral forms, the former of which is the more stable, the dibromide exists only as the blue tetrahedral monomer. It will, however, absorb two molecules of water and form an octahedral dihydrate. The di-iodide, however, neither forms an octahedral polymer nor will it absorb water to form a dihydrate.

HANTZSCH(2,5) reports that $Co(NCS)_2 . 2Py$ exists in a "violet" stable form and gives the blue form in solution. The structure of this compound will be discussed in a later communication dealing with thiocyanates in general but in confirmation of the octahedral-tetrahedral transition we find that the violet form has a magnetic moment (5·1 B.M.) indicating octahedral co-ordination whereas in solution the moment (4·5 B.M.) is that expected for the blue tetrahedral form (See Table 1). Certain ammines e. g. $CoCl_2 . 2NH_3$ exist in two different forms, but it seems likely that here two different kinds of octahedral co-ordination occur. The two forms of the chloride are violet and pink respectively; both colours suggest octahedral co-ordination and this is supported by the fact that both have magnetic moments greater than 5·0 B.M.(13) Similarly the bromides $Co Br_2 . 2NH_3$ exists in two forms with magnetic moments greater than 5·0 B.M; these also presumably involve octahedrally co-ordinated Co^{II}. For the iodide, $CoI_2 . 2NH_3$ SIDGWICK(5) reports that the blue form is the stable isomer; however, KLEMM and SCHUTH(13) report the existence of two forms of moments 4·57 and 4·55 B.M. The existence of two forms in this instance may well arise from dimorphism for both appear to contain tetrahedrally co-ordinated Co^{II}.

It is suggested that these observations can be explained by assuming that the co-ordination number of the Co^{II} atom is dependent upon the polarizability of the ligands. As developed elsewhere(14), we believe that important as steric effects undoubtedly are on occasions, the most important factor deciding the co-ordination number of a metal atom is the polarizability of the ligand. It is considered that, in accordance with the Pauling Electroneutrality Principle, the metal takes up such

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(13) W. KLEMM and W. SCHUTH, *Z. Anorg. Chem.* **210,** 33 (1933).

(14) N. S. GILL, P. J. PAULING and R. S. NYHOLM, *Nature, Lond.* **182,** 168 (1958); N. S. GILL and R. S. NYHOLM, *J. Chem. Soc.* 3997 (1959).

a number of ligands as will reduce its charge to nearly zero. If the ligand is not readily polarized the charge transfer in each metal-ligand dative bond is relatively small and the larger of 2 possible coordination numbers is to be expected (e. g. Fe^{III} prefers to form $[FeF_6]^{3-}$ with F^- as ligand but $[FeCl_4]^-$ with Cl^-). Then with Co^{II} we can understand why H_2O forms a $[Co(H_2O)_6]^{2+}$ ion whereas the more polarizable Cl^- forms a $[CoCl_4]^-$ ion. In passing from pyridine to ammonia we go from a more to a less easily polarizable ligand and hence the tendency for co-ordination number six to arise can be understood. At the same time it must be borne in mind that ease of packing with NH_3 to form an octahedral complex might be an important factor also. Finally, the existence of the blue, low magnetic moment, presumably tetrahedral form of $CoI_2 . 2NH_3$ as the stable form is apparently due to the greater polarizability of I^- over Cl^-. It is thus apparent that Co(II) will form tetrahedral, or octahedral, or tetrahedral and octahedral complexes depending upon what ligand and what halogen atom is present. As has been pointed out earlier, colour must be used with caution in predicting stereochemistry. Usually one finds that octahedral comlexes are pink (e. g. $[Co(H_2O)_6]Cl_2$) or violet (e. g. $CoCl_2 . 2Py$) whilst tetrahedral complexes are blue (e.g. $[PyH]_2CoCl_4$). However, the colour depends upon the ligand as well as the stereochemistry as is shown by the change of colour as one replaces water by ammonia. A much more important criterion of stereochemistry is the *intensity* of the absorption band, tetrahedral complexes having values about one hundred times those of octahedral.

We now consider other metals in the first transition series. In Table 2 are listed the known complexes of type $M^{II}X_2 . 2Py$ formed by Cr^{II}, Mn^{II}, Fe^{II}, Co^{II} and Ni^{II} and Zn^{II}. The chloride, bromide and iodide have been investigated in most cases but certain complexes could not be prepared (see notes to Table 2). The complexes have been examined, using X-ray powder photography, by Mr. P. PAULING. He finds that the powder photographs divide these into three classes. In Class A we have $FeCl_2 . 2Py$, violet $CoCl_2 . 2Py$, $MnCl_2 . 2Py$, $MnBr_2 . 2Py$ and $NiCl_2 . 2Py$. These are obviously octahedral polymers. Class B has a powder pattern not very different from Class A and includes $CrCl_2 . 2Py$, $CuCl_2 . 2Py$ and $CuBr_2 . 2Py$.

DUNITZ(9) has determined the structure of $CuCl_2 . 2Py$ by X-ray studies of single crystals. He has shown that the structure is similar to that of violet $CoCl_2 . 2Py$ (see Fig. 1) except that *two* of the Cu—Cl bonds are considerably longer than the other two (3·05 Å) as compared with 2·28 Å). As may be seen from Figure 1, the difference between this tetragonal type of complex and the almost regular octahedral ones (Class A) is simply a matter of distortion along the z axis. By suitably elongating the bonds along this axis we pass from an octahedral to a tetragonal structure. This distortion is characteristic of Cu^{II} complexes and has been observed in most Cu^{II} complexes studied so far. It is related to the d^9 non-bonding configuration of the copper atom; $ad_\varepsilon^6 d_{z^2}{}^2 d_{x^2-y^2}$ ground state is expected to give rise to tetragonal arrangement of the ligands. A similar situation is expected for d^4 complexes if the electronic configuration is $d_\varepsilon^3 d_{z^2}^1$. This occurs with chromous complexes and it is indeed found that whilst $CrCl_2 . 2Py$ and $CuCl_2 . 2Py$ are not strictly isomorphous they have very similar X-ray powder patterns. This appears to be the first *complex* compound of bivalent chromium for which the expected tetragonal or square planar arrangement has been demonstrated. Unfortunately the chromous complex undergoes oxidation unless air be vigorously excluded. Nevertheless the determination of μ_{eff} on a fairly pure specimen, or one containing some Cr^{III} for which allowance has been made, leads to a moment of 4·98 B.M., calculated using

$$\mu_{eff} = 2{\cdot}84\sqrt{[\chi_m(T-\theta)]},$$

in good agreement with the expected value for four unpaired electrons. A large θ value ($\sim 40°$) is observed which will be discussed in a later communication dealing with a more detailed study of these chromous compounds. Finally in Class C we have blue $CoCl_2 . 2Py$, $CoBr_2 . 2Py$, $CoI_2 . 2Py$, $ZnCl_2 . 2Py$ and $ZnI_2 . 2Py$. These are clearly tetrahedral. It is of interest to note that of the above metals a regular tetrahedral arrangement is feasible for $Mn^{II}(d^5)$, $Co^{II}(d^7)$ and $Zn^{II}(d^{10})$. The failure to observe tetrahedral co-ordination with the manganese complexes is presumably due to the low electronegativity of the Mn^{II} atom which favours six-co-ordination.

It is of interest to compare the stereochemistry of the metal atom in complexes of the type $MX_2 . 2Py$ with that in the anionic complex ions $[MCl_4]^{2-}$(14). Whilst the $[MnCl_4]^{2-}$, $[CoCl_4]^{2-}$ and $[ZnCl_4]^{2-}$ ions are tetrahedral as expected and the $[CuCl_4]^{2-}$ and $[CrCl_4]^{2-}$ ions are different from these, both the $[FeCl_4]^{2-}$ and $[NiCl_4]^{2-}$ ions are also tetrahedral. The lower co-ordination number in this case leading to a tetrahedral arrangement is apparently due to the higher polarizability of the ligands.

Finally we refer to complexes of the type $MCl_2 . 2Py$ formed by metals other than those of the first transition series. Of elements in the second and third series only Pd^{II} and Pt^{II} need be considered. Both $PdCl_2 . 2Py$(15) and $PtCl_2 . 2Py$(16) are monomeric and are undoubtedly square planar. In Group IIA beryllium forms $BeCl_2 . 2Py$(17); this undoubtedly involves a tetrahedrally co-ordinated Be^{II} atom. Both $CdCl_2 . 2Py$(18) and $HgCl_2 . 2Py$(19) are known. According to McConnell(20) the former is isomorphous with the violet form of $CoCl_2 . 2Py$ and hence octahedral. There is disagreement as to the interpretation of the X-ray data for $HgCl_2 . 2Py$. Dunitz(9) proposed that it is isomorphous with $CuCl_2 . 2Py$ and hence tetragonal whereas Grdenic and Kristanovic(21) prefer to regard the compound as consisting of linear $HgCl_2$ units with pyridine of crystallization. It appears that the two structures involve differences in degree rather than of kind.

In Group IVA Sn^{II}(22) and Pb^{II}(23) form $MCl_2 . 2Py$ derivatives but the crystals are not isomorphous with any of the previously investigated types. This is under-

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(15) F. Krauss and F. Brodkorb, *Z. Anorg. Chem.* **165**, 73 (1927).

(16) A. Hantzsch, *Ber. Dtsch. Chem. Ges.* **59**, 2761 (1926).

(17) R. Fricke and F. Ruschhaupt, *Z. Anorg. Chem.* **140**, 112 (1925).

(18) W. Lang, *Ber. Dtsch. Chem. Ges.* **21**, 1578 (1888).

(19) A. Pesci, *Gazz. Chim. Ital.* **25**, 429 (1895).

(20) J. F. McConnell. Private communication.

(21) D. Grdenic and I. Kristanovic, *Ark. Kemi* **27**, 143, (1955).

(22) H. Stephen, *J. Chem. Soc.* **127**, 1874 (1925).

(23) G. W. Heise, *J. Phys. Chem.* **16**, 373 (1912).

standable since these bivalent atoms have a lone pair of electrons in the valency shell. If monomeric, one expects a distorted tetrahedral arrangement based upon the assumption that the lone pair occupies one of the trigonal positions in a trigonal bipyramidal arrangement. If dimeric, each metal atom will be five covalent, the stereochemistry being based upon an octahedron, a lone pair occupying one of the six positions. Unfortunately molecular-weight measurements to enable us to distinguish between these are not practicable.

TABLE 2.—COMPLEXES OF FIRST TRANSITION SERIES

No. of non-bonding *d* electrons	Compound	Colour	Magnetic moment of solid	Stereo-chemistry
4	$CrCl_2.2Py$ $CrBr_2.2Py$	green green	4·66 4·43	tetrahedral
5	$MnCl_2.2Py$ $MnBr_2.2Py$	pink pink	5·89(24) 5·96(24)	octahedral
6	$FeCl_2.2Py$	yellow	5·75	octahedral
7	$CoCl_2.2Py$	violet	5·15	octahedral
		blue	4·42	tetrahedral
	$CoBr_2.2Py$	blue	4·50	tetrahedral
	$CoI_2.2Py$	green-blue	4·47	tetrahedral
8	$NiCl_2.2Py$	yellow-green	3·37	octahedral
9	$CuCl_2.2Py$	blue	1·85	tetrahedral
	$CuBr_2.2Py$	green	1·79	tetrahedral
10	$ZnCl_2.2Py$	white	diamag.	tetrahedral
	$ZnI_2.2Py$	white	diamag.	tetrahedral

(24) R. W. ASMUSSEN, *Symposium on Coordination Chemistry* p. 27, Copenhagen (1953).

Also prepared: $Mnpy_4I_2$; $Nipy_4Br_2$; $Nipy_4I_2$

$FeBr_2$+pyridine appears to give $Fepy_4Br_2$ (yellow) which continuously loses py and analysis figures were between those for $Fepy_4Br_2$ and $Fepy_2Br_2$. Loss of py does not stop at $Fepy_2Br_2$.

FeI_2+pyridine gave a compound which continuously loses py and final analysis fitted no definite formula but contained not more than 1 py—it appears that what happens is $Fepy_6I_2$ (yellow) → $Fepy_4I_2$ (brown) → finally brown compound containing 1 py per Fe. $Crpy_2Br_2$—not analysed but very similar to Cl compound.

EXPERIMENTAL

All compounds but one have been previously described, some a number of times, and therefore the analyses are not reported. They were prepared by reacting the metal halide (1 mole) with pyridine (2 moles) in ethyl alcohol and recrystallized from ethyl alcohol when possible. The exceptions were bis-pyridine dibromo manganese(II), bis-pyridine dichloro chromium(II), bispyridine dichloro nickel(II) which were not recrystallized, the manganese complex undergoes slight oxidation when recrystallized; bis-pyridine dichloro copper(II) was recrystallized from dimethylformamide. *Bis-pyridine diaquo dibromo cobalt*(II). On standing in air, bis-pyridine dibromo cobalt(II) took up two molecules of water and became violet in colour. The water could be removed on standing in a desiccator over a drying agent. (Found: C, 29·1; H, 3·5. Calc. for $C_{10}H_{10}Br_2CoN_2 . 2H_2O$: C, 29·1; H, 3·4 per cent).

Magnetic susceptibilities were determined by the Gouy method.(25) Absorption spectra were obtained with a Unicam SP–500 spectrophotometer.

Acknowledgement—One of us (N. S. G.) acknowledges the award of a Turner and Newall Research Fellowship at University of London and held at University College where this work was carried out.

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(25) B. N. Figgis and R.S. Nyholm, *J. Chem. Soc.* 331 (1959).